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(54) IMPROVEMENTS IN OR RELATING TO DIFFUSION COATING OF METALS

(71) We, OFFICE NATIONAL D'ÉTUDES ET DE RECHERCHES AEROSPAZIALES (par abréviation O.N.E.R.A.) a French Body Corporate, of 5 29 Avenue de la Division Leclerc, 92-Châtillon-sous-Bagneux, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the diffusion coating of metals, and particularly the introduction of aluminium into the surface of high 15 temperatures superalloys. Such coating is described, for example in United States Patents Nos. 2,875,090 and 3,226,207 and in French Patent No. 1,490,744, and other metals, such as chromium and/or silicon and/or iron, 20 may be diffused into the surface along with the aluminium.

Diffusion coating of high temperature 25 superalloys is generally carried out at very high temperatures, around 980°C. and in a closed container that need not be sealed. The coating, therefore, spreads over all the metal surfaces in the container, including the container walls. It is often necessary to keep the coating from some portions of the workpieces, for example, jet engine turbine blades 30 must have uncoated roots if their assembly dimensions are to be kept within tolerance. Also, welded areas can be adversely affected by diffusion coating and are, advantageously, 35 masked.

Shielding the root from the diffusion while exposing the remainder of the blade being coated is a difficult task, particularly when a quantity of the blades is treated simultaneously in the same container. The atmosphere within the container becomes a very penetrating coating medium that tends to pervade everything in the container. Shielding or masking materials may be swamped and 40 rendered ineffective, or if very active, tend 45

to cause undesired changes in the surface of the substrate.

It is an object of the present invention to provide novel techniques for confining the foregoing diffusion of aluminium, and of any other metal, to desired locations. A further object is to provide improved materials and processes for diffusion coating.

According to the present invention there is provided a process for the formation of a diffusion surface alloy on a part of a metal object by the make-up of at least one metal, in which process the object is treated in a reactive coating composition containing the or each make-up metal, the part or parts of the object on which no diffusion surface alloy is to be formed being shielded by a masking composition comprising at least one aluminide. The invention advantageously provides a process for the formation of a diffusion alloy on a part of an object made of a cobalt- or iron-based superalloy by the make-up of at least aluminium, in which process the object is treated in a reactive coating composition containing the or each make-up metal, the part or parts of the object on which no diffusion surface alloy is to be formed being shielded by a masking composition comprising a cobalt aluminide and/or a nickel aluminide, the or each aluminide having a formula such that the proportion of aluminium per cobalt or nickel atom is in the range of from 0.25 to 1 atom.

According to a preferred embodiment of the present invention, cobalt and nickel aluminides containing less than one atom of aluminium for each atom of cobalt or nickel provide very effective masking of aluminium diffusion, as well as the diffusion of other metals, into superalloys. The diffusion of the aluminium is also simplified by the use of a cementation pack in which the aluminium is in the form of particles of aluminium-chromium, aluminium-silicon, aluminium-chromium-silicon or aluminium-chromium-

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Sheet 2

Fig. 3.

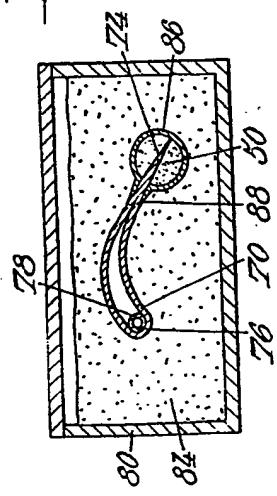
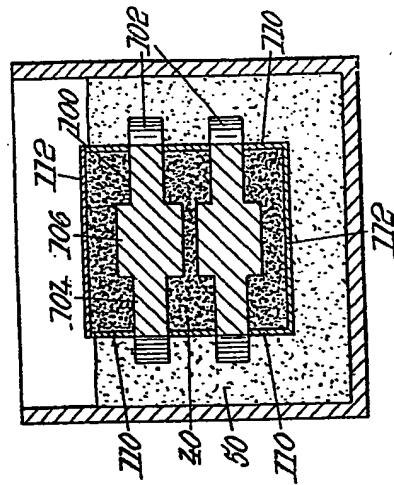
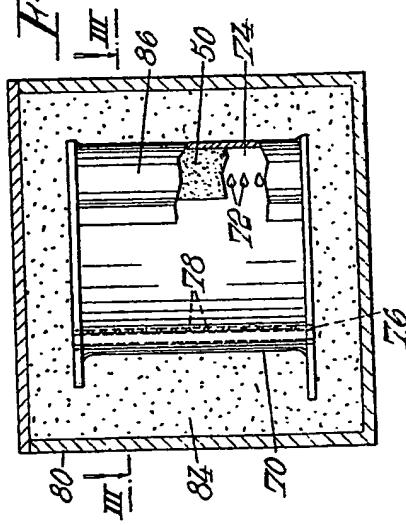


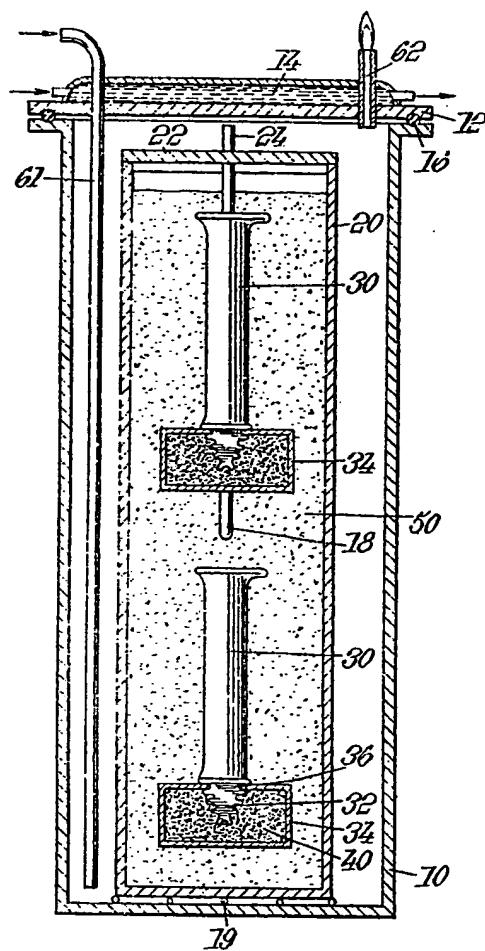
Fig. 2.



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Sheet 1

Fig.1.



wherein the masking slurry contains an agglomerating agent.

5 13. A process according to any one of the preceding Claims, wherein a fine alloy powder is used as active ingredient in a reactive composition, the powder-form mixture of reducible compounds of the metals required to form the alloy powder having been reduced magnesothermically.

10 14. A process according to Claim 13, wherein at least one of the reducible compounds was an oxide.

15 15. A process according to Claim 14, wherein at least one of the reducible oxides is chromium, aluminium or silicon oxide.

16. A process, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawing.

20 17. A process, substantially as hereinbefore described with reference to Figures 2 and 3 of the accompanying drawing.

18. A process substantially as hereinbefore described with reference to Figure 4 of the accompanying drawing.

19. A process, substantially as described in foregoing Example I.

20. A process, substantially as described in foregoing Example II.

21. A process, substantially as described in foregoing Example III.

22. A process, substantially as described in foregoing Example IV.

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- mic reduction. 1000 grams of magnesium was melted in a steel retort under argon. After cooling to room temperature, 200 grams of Cr₂O₃ powder, 200 grams Fe₂O₃ powder and 50 grams Al₂O₃ powder was placed on top of the solidified magnesium melt. The retort was covered with a semi-tight steel lid and this assembly placed in an Inconel outer retort. A low flow of argon gas, utilising a flow rate of 6 c.f.h. (170 litres per hour) was passed through the Inconel retort thereby blanketing the internal steel retort containing the magnesium and mixed oxides. The Inconel retort was then heated to a temperature of 982°C and maintained at this temperature for nine hours. After this time, the retort was cooled to room temperature in the argon atmosphere. The product was removed from the retort, crushed, and reacted with a solution of nitric acid containing one part by volume of 67% commercial nitric acid and one part by volume of water. Enough nitric acid was utilised to be 25% in excess of that required to combine with all the magnesium originally present. Since the action of nitric acid on the reacted powder was quite exothermic, it is helpful to have a water cooling jacket on the reaction kettle. Upon completion of the leaching process, the resulting alloy powder was washed thoroughly to a neutral pH, vacuum filtered using a Buchner funnel and chamoic filter pad, dried in an oven at 177°C for four hours and pulverised. The powder contained 44% Cr, 47% Fe and 9% Al. Another such alloy contained 25% Cr, 5% Al, the balance Fe, and was also a good diffusion coating composition. Any such alloy containing 3 to 15% Al and 12 to 60% Cr, the balance Fe, gives very good coating on superalloys.
- The addition of about 0.2% yttrium to the iron - chromium - aluminium alloys further improves them.
- Clearly, and as the foregoing shows, the invention is not limited to that of its uses nor to those embodiments of the various parts which have been more particularly described, except as defined in the following claims.
- 50 WHAT WE CLAIM IS:—**
1. A process for formation of a diffusion surface alloy on a part of a metal object by the make-up of at least one metal, in which process the object is treated in a reactive coating composition containing the or each make-up metal, the part or parts of the objects on which no diffusion surface alloy is to be formed being shielded by a masking composition comprising at least one aluminide.
 2. A process for the formation of a diffusion surface alloy on a part of a metal object by the make-up of at least one of aluminium, chromium, silicon and iron in which process

the object is treated in a reactive coating composition containing the or each make-up metal, in a halogenated atmosphere, the part or parts of the object on which no diffusion surface alloy is to be formed being shielded by a masking composition comprising at least one aluminide.

3. A process for the formation of a diffusion alloy on a part of an object made of a cobalt or iron-based superalloy by the make-up of at least aluminium, in which process the object is treated in a reactive coating composition containing the or each make-up metal, the part or parts of the object on which no diffusion surface alloy is to be formed being shielded by a masking composition comprising a cobalt aluminide and/or a nickel aluminide, the or each aluminide having a formula such that the proportion of aluminium per cobalt or nickel atom is in the range of 0.25 to 1 atom.

4. A process for the formation of a diffusion alloy on a part of an object made up of a cobalt- or iron-based superalloy by the make-up of at least aluminium, in which process the object is treated in a reactive coating composition containing the or each make-up metal, the part or parts of the object on which no diffusion surface alloy is to be formed being shielded by a masking composition comprising nickel aluminide containing at least one atom of aluminium per atom of nickel.

5. A process according to Claim 3 or 4, wherein the masking composition comprises at least one nickel aluminide having a formula in the range Ni₃Al to Ni₄Al.

6. A process according to any one of the preceding claims, wherein the masking composition comprises a mixture of finely divided aluminide(s) and an inert substance which does not stick to the surface with which it is in contact during the diffusion treatment.

7. A process according to Claim 6, wherein the inert substance is alumina.

8. A process according to Claim 7, wherein the proportion of alumina by weight in the masking composition is from 25 to 66%.

9. A process according to any of the preceding Claims, wherein the part(s) of the objects which are required not to be diffusion-treated are placed in the masking composition, the whole being placed in the reactive coating composition.

10. A process according to Claim 9, wherein the masking composition is isolated from the reactive coating composition by a trough.

11. A process according to any of Claims 1 to 8, wherein the masking composition is prepared in the form of a slurry with which the part(s) not to be diffusion-treated are masked.

12. A process according to Claim 11,

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also helpful in the diffusion treatment of superalloy substrates to which a layer of diffusion coating material is adhered, as in U.S. Patent 3,312,546. Such a layer of powdered aluminium - chromium - iron alloy in lacquer, for example, is removed from, or not applied to, the areas to be masked and the masking composition applied there instead. When a halide-free atmosphere is used during the diffusion, no masking composition need be applied to the areas in which the diffusing alloy is not present.

The foregoing coating techniques are equally effective for unrestricted or masked coating of nickel-, cobalt-, or iron-base alloys suitable for use under stress at temperatures of 870°C or higher. Such alloys are generally called superalloys and include those in which the principal ingredient or base is a mixture of any one, two or all three of the metals nickel, cobalt and iron. An example of the latter is an alloy containing equal parts by weight of nickel, cobalt and iron. The base content of the superalloys can vary from as much as 70% or even 98% if thoria-dispersed nickel is considered an alloy, to as little as about 50%. A list of typical superalloys is included in French Patent 1,490,744. Even ordinary stainless steels such as one containing 18% Cr and 8% nickel can be generally effectively provided with good aluminium-rich coatings pursuant to the present invention, and will then generally show great resistance to oxidation at 1040°C, although such alloys are not suitable for use under stress at that temperature.

The preferred coatings of the present invention are diffused from alloys of aluminium and chromium in which the chromium content by weight is four to five times the aluminium content. Also, the coating composition as well as the masking composition should contain from about 1/4 to about 2/3 of an inert diluent, such as alumina, that does not tend to sinter to the workpieces and also keeps the remainder of the composition ingredients from sintering to the workpieces. In addition to the alumina and magnesia referred to above, Cr_2O_3 , ZrO_2 and TiO_2 may be so used. Diluents that tend to be chemically reduced by or react with hydrogen or composition ingredients at the coating temperatures, are not desirable.

The circulation of hydrogen, discussed in connection with Figure 1, is not essential since argon or any other protective gas can be used in its place, although hydrogen seems to give somewhat better coatings and it is more easily monitored because of its combustibility. Indeed, it is not necessary to circulate any gas around the inner retort, although hydrogen may then tend to accumulate in the space between the retorts. Such accumulation may form an explosive mixture

with air, if a flushing of the gas in the inter-retort space is not performed. 65

It is necessary to activate the coating composition to keep the coating temperatures and times within reasonable limits. Ammonium halides, and particularly the chloride, 70 are very effective additions to the composition for this purpose, and they need only be used in an amount from about 0.1% to about 1%, preferably 0.2 to 0.6% of the composition by weight. Ammonium fluoride, bromide and iodide are more expensive and more difficult to handle, and so are not preferred, although ammonium bromide works better than the fluoride or iodide. Other halides such as aluminium chloride, chromic chloride, 75 chromous chloride and even the halogen acids or the halogens themselves can be used, although those activators that are gaseous are more difficult to load in the inner retort. The activator need not be loaded at the time the work is, however, but may be added after the inner retort is closed, for example by providing a conduit in the lid of that retort and introducing gaseous or liquid activator through the conduit after the work has been brought to coating temperature, for example. 80 As pointed out above, such a fitted conduit may also be used with solid activators that are pre-mixed with the composition, and it will then simplify the flushing out of air from 85 the pack as the activator vaporises. 90

The use of a cover over the inner retort reduces the amount of activator needed by limiting the amount that escapes during the heat. Where larger losses can be tolerated, the 100 cover may be omitted, particularly if the flushing is restricted or completely eliminated. The inner retort may be alternatively fitted with a liquid-sealed lid as described, for example, in U.S. Patent 2,844,273. The 105 outer retort may also be omitted.

The nickel - aluminide masking of the present invention generally works well with all of the above-mentioned superalloys. Cobalt aluminide does not do a good job of masking nickel-based superalloys or superalloys containing as much as 25% nickel, although it is quite effective for masking cobalt- and iron-based superalloys. 110

Incoloy 800 is an example of an iron-based 115 superalloy suitable for masked as well as unmasked coating pursuant to the present invention. This alloy is composed of 32% Ni, 0.04% C, 20.5% Cr, 0.75% Mn, 0.0007% S, 0.35% Si, 0.3% Cu, 0.3% Al, 0.3% Ti, the balance Fe, and exhaust manifolds of this material treated at 1065°C for 8 hours with the coating composition as in Example I have a coating case depth of 5 miles (125 microns), except where masked by a $\text{Ni}_3\text{Al}_3-\text{Al}_2\text{O}_3$ masking composition. 120

A very satisfactory iron - chromium - aluminium coating alloy pursuant to the present invention was prepared by magnesother-

- the relatively volatile magnesium metal remaining after the reduction is completed, the crude reaction product can after crushing be directly used for diffusion coating.
- 5 Where nitric acid washing is carried out, the washed material is rinsed with water, preferably to neutrality, filtered and dried before use.
- Magnesothermic reduction may also be used in the same way to directly produce chromium - silicon, chromium - aluminium - silicon, chromium - aluminium - iron, molybdenum - silicon and tungsten - silicon alloys in the extremely finely divided form so highly desirable for diffusion coating workpieces. Silica makes a convenient source of silicon for such purposes and may be directly substituted for or added to the mixture being reduced without materially changing the reduction rate or temperature. The finely divided alloys may also be produced magnesothermically reducing chromium, iron, molybdenum or tungsten oxides or other compounds of these metals in the presence of aluminium and/or silicon in elemental form. During such reduction the aluminium and/or silicon alloys with the metallic chromium, iron molybdenum or tungsten as it is formed.

Example III

- 30 The arrangement described in connection with Figures 2 and 3 was prepared with a coating composition 50 as described in Example I, the supporting pack 84 being entirely calcined alumina, and the vane 70 being Wi-52 alloy. The coating heat was effected at 1080°C for 16 hours, after which the vanes showed a uniform coating of about 0.0015 inch (0.038 mm) thickness throughout the surfaces in contact with the coating composition, with a slight throw of the coating about 1/16 to 1/8 inch (1.6 to 3.2 mm) further. This throw can be kept from the machined areas by, for example, using the above-mentioned masking compositions in a layer about 1/8 inch (3.2 mm) thick or thicker against the portions of the workpiece surface adjacent the coating composition and extending as far from it as the coating tends to otherwise throw.

Example IV

- 50 Turbine wheels as illustrated in Figure 4, having an overall diameter of 9-1/4 inches (23.5 cm), a body diameter of 7-1/4 inches (19 cm) and having an air-foil cup width of 3/4 inch (19 mm) were assembled with masking and coating compositions as in that Figure. The wheels were of MarM 246 (r. Trade Mark) alloy containing by weight 9% Cr, 10% Co, 1.5% Ti, 5.5% Al, 2.5% Mo, 0.15% Fe, 10% W, 1.5% Ta, the balance being nickel. The coating composition was the same as used in Example I, the masking composition was that of Example I except

that the Ni-Al alloy corresponded to Ni₃Al, and the coating heating was effected for seven hours at 1032°C. The case depth produced was 0.0025 inch (0.0635 mm), with no coating of the masked areas.

It is preferred for the masking composition to be in finely divided form such as powder particles no greater than about 30 mesh and better still smaller than 40 mesh, since they then present a large surface area to the coating atmosphere. However larger particle sizes may be used.

The masking of the present invention is also effective when the diffusion coating is carried out with a composition which is entirely inert, but through which coating vapours are passed, as disclosed in U.S. Patent 3,286,684. In fact, the entire coating composition may be eliminated, and vapours alone used, particularly where the masking composition is adequate to support the workpieces. Correspondingly, where localised coating is effected as in Figure 2 and the workpieces may be adequately supported by the local coating composition, the remainder of the support may be omitted. However, the coating composition tends to throw when an inert support is not used.

The masking of the present invention may also be effected by adding the masking composition as a slurry to a container in which the workpiece is supported. The slurry may be an aqueous suspension, and the water content permitted to drain off so that the solids of the slurry remain, in which the workpiece remains embedded. The draining of the water is simplified by providing the container with a larger number of small perforations that do not permit much of the slurry solids to pass through.

The slurry may also be poured into a container in which the workpiece is already supported by an inert coarse alumina, 100 mesh for example. By having the slurry solids in the form of very fine powder, the slurry will be absorbed by the coarse alumina and convert it to a very efficient mask.

The slurry may also contain thickening or setting agents such as gum tragacanth and bentonite, so that the workpiece is more effectively supported by the slurry with or without the inert coarse alumina. One composition of this type has by weight 69% of a 325 mesh powder half Al₂O₃, and half Ni₃Al, and 31% of a solution of 0.7% gum tragacanth in 1.7% ethanol and 97.6% water. This composition is a paste into which a workpiece can be forced so that it stays in place while the composition is dried and is continued to be held in place during a firing and a diffusion coating heat treatment. Thickening and setting agents so used should be decomposable by such high temperatures, or inert to the diffusion treatment.

The masking of the present invention is

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of the masking composition rendered the masking ineffective to prevent completely diffusion coating of the blade roots. The substitution of nickel alone for the alloyed material maintained the masking effectiveness but weakened the blade roots, apparently due to excessive depletion of chromium and/or other ingredients from the skin thereof during the coating treatment.

Masking results similar to that produced by the aluminide Ni₃Al were also obtained using nickel aluminides ranging from Ni₃Al to those having only slightly less aluminium than Ni₃Al. With nickel contents larger than Ni₃Al, the weakening of the masked portions became significant and treatment with such alloys was found not to be desirable. The preferred range is from Ni₃Al to Ni₃Al₂.

Example II

Jet nozzle guide vanes 3-3/4 inches long and similar to those illustrated in Figures 2 and 3, but without cooling tubes 76, were diffusion coated with the same coating composition 50 used in Example I. The vanes were of Wi-52 alloy having a composition by weight of 21% Cr, 0.45% C, 1.8% Fe, 11% W, 2% Co plus Ta, the balance being cobalt. The interiors of the vanes were filled with the coating composition but that composition was kept from contacting the mouth of the opening leading to the interior of the vane. The opening was in a buttress position of the vane and the mouth is used as a site for welding on a cooling tube. The edge wall of the mouth was accordingly masked with a layer of masking composition poured over the coating composition 50 filling the vane's interior. A cap may also be used below and/or above the layer of masking composition, but this was not essential unless the masking layer was not level and needed supporting to stay in place. The masking composition used was a mixture of equal parts by weight of minus 325 mesh alumina, and a similarly sized crushed cobalt-aluminium-alloy made by heating powdered cobalt and aluminium for six hours at temperature of 1010°C, under hydrogen, in the proportion of three gram-atoms of cobalt to one gram-atom of aluminium, the outer faces of the vane's buttresses need not be coated so that the masking layer may be thicker than needed to protect the mouth of the opening into the vane's interior. The coating was applied by heating for twenty-hour at a temperature of 1082°C, developing a case depth of 0.002 inch (0.05 mm). After removing the coated vanes from the inner retort, freeing them from the coating and masking compositions, and washing, the masked areas were bright and silvery and free of coating, the remainder being bright bronze-coloured.

The masking compositions of Example I and II may be reused although it is preferred

to separate and discard the portion of the composition which was in contact with the masked surface. About 1/8 inch (3.2 mm) depth of such portion should generally be so discarded.

The coating composition 50 may also be reused, preferably after adding a small amount of fresh chromium and aluminium or pre-fired chromium-aluminium alloy to replace that consumed by the coating operation. Some of the ammonium chloride is also lost during the coating, and this loss is desirably made up before reuse. Instead of using a separate firing step to prepare the make-up chromium-aluminium alloy, a make-up quantity of an unfired chromium-aluminium alloy may be added to the very top of the coating composition so that during the coating step it is at least about an inch from the nearest surface to be coated. The high temperature of the coating operation will serve to pre-fire the unfired portion so that it can be incorporated in the body of the coating composition when it is reused. During a coating step, consumption of aluminium is, on a weight basis, two or five times as much as the consumption of chromium, so that it is desirable to have the make-up quantities of these metals in the same proportions.

The separate step of pre-firing the chromium and aluminium alloy may be avoided by directly preparing such alloy in finely divided form. To this end, the magnesothermic reduction of chromium compounds, such as Cr₂O₃, as described in French Patent 1,123,326 and its Addition Patent 70,936, may be modified by combining an appropriate quantity of alumina with the chromium compound, and such combination mixed and subjected to the magnesothermic reduction as described in those patents. This simultaneous reduction takes place at about the same temperatures and times as is shown for the reduction of the chromium compound alone and with the same equipment, producing a chromium-aluminium alloy having a particle size of about 1 micron. Residual magnesium as well as magnesium oxides present in the reduced material is removed by treatment with an excess of dilute nitric acid having a specific gravity of about 1.12 to about 1.26. Such acid will not attack chromium-aluminium alloys having as little as 16% chromium by weight, but will readily dissolve metallic magnesium as well as magnesium oxide. Crushing the alloy to a fine powder helps the acid dissolve all the magnesium rapidly. It is not essential to remove any magnesium oxide present in the reduced mixture inasmuch as this compound is essentially inert during a coating operation and does not tend to sinter or adhere to the work-pieces being coated or to the other ingredients of the coating composition. Where the magnesothermic reaction mixture is flushed through at high temperatures to flush out

metal, such as Inconel 600 or Incoloy 800. The word "Inconel" and the word "Incoloy" are Trade Marks.

Referring now to Figures 2 and 3, there is illustrated a selective coating arrangement in which only a small portion of a jet engine vane 70 is diffusion coated. The vane 70 is hollow and has cooling passageways 72 at its trailing edge as well as a welded-in cooling tube 76 with narrow discharge perforations 78 along its length. The trailing edge is quite thin and needs coating because rough handling has caused the spalling off of an originally applied coating. Because of the narrow size of the air outlet perforations 78, they cannot be exposed to coating conditions without having the coating deposit on the mouths of the perforations, which would unduly restrict them. To avoid having to remove and later replace the cooling tube, recoating may be effected in a localised area in the manner illustrated.

For this purpose, one or more vanes 70 are fitted in an inner retort 80 where each is embedded in a particular material 84 that may merely be an inert supporting material such as powdered alumina. Before embedding, the trailing edge 74 of each vane is inserted in a slot 88 of a tubular holder 86 and the holder filled with a diffusion coating composition 50. The holder 86 is shaped to extend just beyond the outer openings of the cooling passageways 72. It is not necessary to have the lips of the slot 88 engaging the vane, and a clearance of as much as 1/16 to 1/4 inch (1.6 to 6.4 mm) may be provided at each lip, so long as the powdered contents of the holder do not spill out. The thickness of the coating composition 50 contacting the vane surface should be at least about 104 inch (6 mm) within about 1/4 inch (6 mm) of all surfaces to be coated, to assure the presence of sufficient coating composition.

Figure 4 illustrates the partial coating of turbine wheels 100 having a number of peripheral fins 102 projecting from the outside of a body portion 104 provided with a central hub 106. The only parts exposed in use to the hot impelling gases are the fins 102 and the outside surface of the body portion 104 between the fins 102, and these are the only parts to be diffusion coated. This avoids changing the dimensions of the remaining surfaces as well as changes in strength of those highly stressed portions. Such restricted coating is effected by stacking the wheels between masking rings 110 that have the same outer diameter as the body portions 104 of the turbine wheels 100 and hold masking compositions 40. The stacking is readily effected by first placing a turbine wheel 40 with its axis vertical on a support, stacking a ring 100 over it, filling the ring with masking composition, covering the filled ring with

a plate 12, clamping the assembly together, inverting it, and placing the inverted assembly in a retort containing a supporting layer of coating composition 50, removing the clamps, placing a second ring 110 over the top of the inverted turbine wheel 40, filling the second ring 110 with masking composition, and stacking more turbine wheels 40 and rings 110 on top of the second ring. The uppermost ring 110 may be covered by another plate 112, although this is not essential, and the retort filled with coating composition 50.

The following Examples illustrate the invention.

Example I

Using the arrangement of Figure 1, 180 jet turbine blades of B1900 alloy having an overall length of about 4-3/8 inches (111 mm) were loaded in troughs 34, thirty to a trough and six layers of such troughs loaded in a diffusion retort. The B1900 alloy has a composition by weight of 8% Cr, 10% Co, 1% Ti, 6% Al, 6% Mo, 4.3% Ta, 0.15% B and 0.01% Zr, the balance being nickel. The blade roots were embedded in a mixture of equal parts by weight of minus 325 mesh calcined alumina and approximately the same size powdered nickel-aluminium alloy formed by heating for eight hours at 982°C under hydrogen, a mixture of two gram-atoms of nickel and one gram-atom of aluminium. The heated product is a brittle alloy that corresponds to the nickel aluminide, Ni₂Al.

The diffusion coating reactive composition 50 was a pre-fired mixture of 1-micron size chromium powder, minus 325 mesh (about 17 micron average) aluminium powder, minus 325 mesh calcined alumina, and ammonium chloride as described in Example 1 of French Patent 1,490,744. The retort assembly was heated to 1065°C in a gas-fired furnace and maintained at this temperature for six hours while a stream of hydrogen was passed through the space between the retorts and burnt as it emerges. Water was also circulated through the outer cover 12 to prevent it getting too hot.

After the heating was completed all the retorts were cooled, disassembled, the coating composition 50 removed by suction, and the blade-carrying troughs lifted out as they were exposed. The blades showed very good coatings about 0.003 inch thick on all parts that had been in contact with the coating composition 50, the coating tapering off to nothing within about 1/8 inch (about 3 mm) of where the roots had rested against the trough surface. The roots showed no dimensional, metallurgical or strength changes and passed the same fatigue tests as the untreated blade.

Substituting an unalloyed nickel and aluminium mixture for the nickel aluminide

iron alloy about 1 micron in size. Such particles are conveniently produced by magnesothermically reducing a mixture of reducible compounds of aluminium and of the other metal(s) of the alloy. The oxides of the various metals are particularly suitable for magnesothermic reduction.

The term "metal object" as used herein includes refractory metal objects.

For a better understanding of the invention and to show how the same may be put into effect, reference will now be made, by way of example, to the accompanying drawings in which:—

Figure 1 shows a vertical sectional view of a diffusion apparatus for use in the process of the present invention,

Figures 2 and 3 show vertical and horizontal sectional views, respectively, of a modification of the diffusion apparatus of Figure 1, and

Figure 4 shows a fragmentary view of a further modification of the diffusion apparatus of Figure 1.

Referring now to the drawing which illustrates masking arrangements pursuant to the present invention, Figure 1 shows an outer metal retort 10 having a bolt-on cover 12 equipped with a water-circulating jacket 14 and an O-ring seal 16. The retort 10 receives an inner metal retort 20 covered by a loosely fitting lid 22. The inner retort 20 is almost completely filled with the diffusion coating materials including coating reactive composition 50 and work pieces to be coated, shown as an example, as jet engine blades 30, held in two rows in individual carriers 34. Each carrier 34 is an elongated metal trough having a longitudinal slot 36 in its upper wall.

A row of blades 30 is fitted into the slot with blade roots 32 therebelow, the remainder of each blade 30 being above the slot 36. The trough can be readily fashioned from sheet metal bent to form a slot of the correct width for the particular blades to be treated.

The blade roots 32 are embedded in a masking composition 40 which is a powdered mixture containing one or more of the above-mentioned aluminides and may be poured into the troughs through the open ends thereof after the blades 30 are all mounted. The open trough ends can then be closed, for example by bending the trough bottom or side walls. The closing need not be a complete

sealing of the ends so long as the masking composition is kept in place during the loading of the inner retort. The individual blades 30 in a trough are preferably spaced from each other and there is no need to isolate the masking composition from contact with the surrounding coating composition 50 in the spaces. If desired, a separator such as a metal sheet may be interposed between the masking position and the coating composition where they would otherwise come in con-

tact with each other. This helps keep the two compositions separate when the retort is emptied so that each may be more readily reused. The separating sheet can be plain carbon steel or a type 400 stainless steel where the atmosphere in the coating retort is high in hydrogen or other reducing agents. Should that atmosphere lack sufficient reducing ability then it is preferred to have the interposed sheet of the same material as the workpieces being coated.

The retort 20 may be loaded by first pouring in a layer of diffusion coating composition 50, then inserting a layer of one or more previously prepared and filled troughs 34, then pouring in additional coating composition 50 to cover the through layer and its content, following which another layer of troughs may be inserted, and the steps repeated until the retort is filled to the appropriate level. The lid 22 is then applied either as a loose fit or it may be sealed, for example by being welded on, in which case it is desirable to leave a little space at the top of the inner retort so that particles of the coating composition do not interfere with the welding. Where the inner retort is sealed with a welded-on cover, it is desirable to provide a conduit through the cover or wall of the retort through which the internal pressure can be monitored and controlled.

The inner retort 20 of Figure 1 is shown loosely covered and inserted in the outer retort 10, a lifting ring 24 welded to the outer surface of the inner retort providing a convenient lifting arrangement for this purpose. The inner retort 20 is shown as not filling the outer retort 10, gas introduction and discharge tubes 61, 62 being arranged in the space thus provided. Thermocouples such as the one shown at 18 in a thermal wall, as well as others in internally projecting pockets may also be fitted to appropriate locations in or on the inner retort 20 and provided with leads extending through the cover 12 to convenient reading and recording instruments. A supporting spider 19 may be placed on the floor of the outer retort 10 to receive the bottom of the inner retort 20.

The retort assembly, with the cover 12 tightly secured, is now lowered into a furnace where it is heated to coating temperature, generally between about 870° and 1260°C., and kept there for the desired coating time. A blanketing gas such as hydrogen, is flushed through the tubes 61, 62 and burned as it emerges.

The retorts and the troughs should be of material that withstands the furnace temperatures. Ordinarily mild or low carbon steel is adequate for the inner retort 20 and troughs. The outer retort 10 has its exterior exposed to air during the coating operation and should therefore be of oxidation-resistant

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